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MEMORANDUM FOR PRS (Contractor Pu

7 October 1999

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-~~FY99~~ 1999-0184**, Ismail Ismail, ERC, and Tom Hawkins, PRSP, "Physical and Chemical characterization of Ultrafine Aluminum Powders"

(Statement A)

ACS Pacific Conference on Chemistry and Spectroscopy, 6-8 Oct 99

PHYSICAL AND CHEMICAL CHARACTERIZATION OF ULTRAFINE ALUMINUM POWDERS

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and

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INTRODUCTION

- **Compared to "regular" aluminum powders, ultrafine aluminum UFAl enhances the burning rate of propellants.**

- **Smaller UFAl particles have a large surface area which enhances the burning rate, they also have a large percentage of Al_2O_3 which reduces the ISP of the propellants.**

- **Open literature indicates UFAl powders can be prepared by several methods:**
  - **Electro-explosion of metal wires: Argonide Corporation** (www.argonide.com)
  - **Plasma torch vaporization & condensation** (dol1.eng.sunysb.edu/tsl/ctsr/nuggets/nugget1/).
  - **Catalytic thermal decomposition of AlH_3 adducts** (MRS 457, 131, 1997).

BACKGROUND

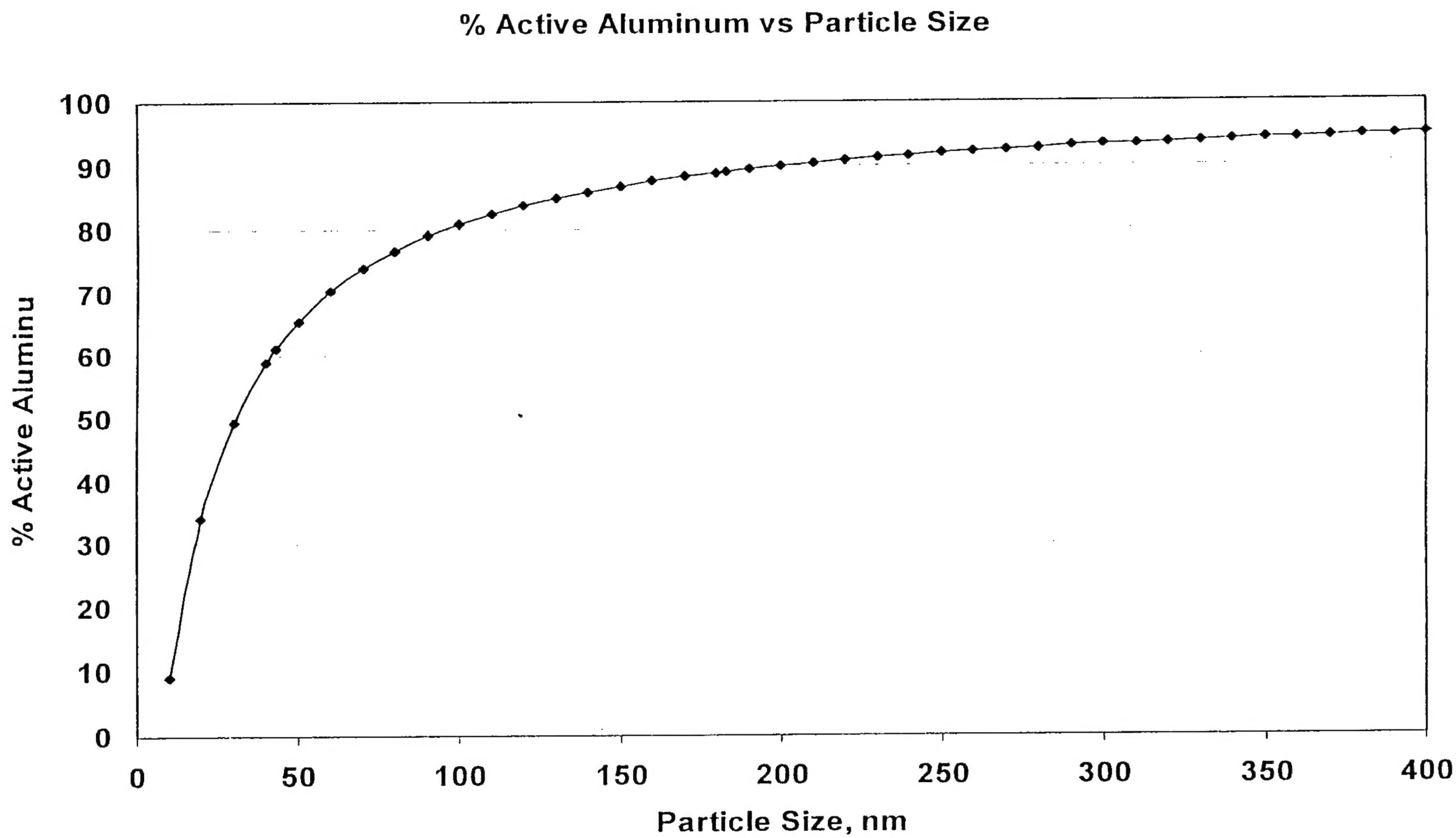
- Metallized gelled propellants such as O_2/RP-1/Al and gelled hydrogen O_2/H_2/Al have been considered by NASA - nanoparticulate gellants by NASA/TRW (www.grc.nasa.gov/WWW/TU/launch/China)
- With UFAl powders, there is a potential for reduced gellant masses and agglomeration on nozzle.
- Higher rocket performance is needed for future missions.
- Different sources (DOD, NASA and private sector) have confirmed that the addition of UFAl powder to propellants increases burning rate by as much as a factor of 3.
- Open literature sites many methods of preparations but less emphasis has been given to properties of ultrafine particles.
- Due to their low bulk density, the powders are difficult to handle and their characterization is a challenge.

OBJECTIVES

- **Develop techniques and methodologies for physical and chemical characterization of UFAl powders.**
- **Characterize the powders obtained from different sources.**
- **Develop a methodology to study the kinetics of reactions between UFAl and oxygen (oxidation) or nitrogen (nitridation) at different conditions.**
- **Estimate diffusion parameters and limitations for the reactions.**
- **Determine composition and crystallographic structure of solid residues left after the oxidation and nitridation reactions.**
- **Generate simple computer models to address the thickness of pre-existing Al_2O_3 layer on the particles of UFAl powders.**

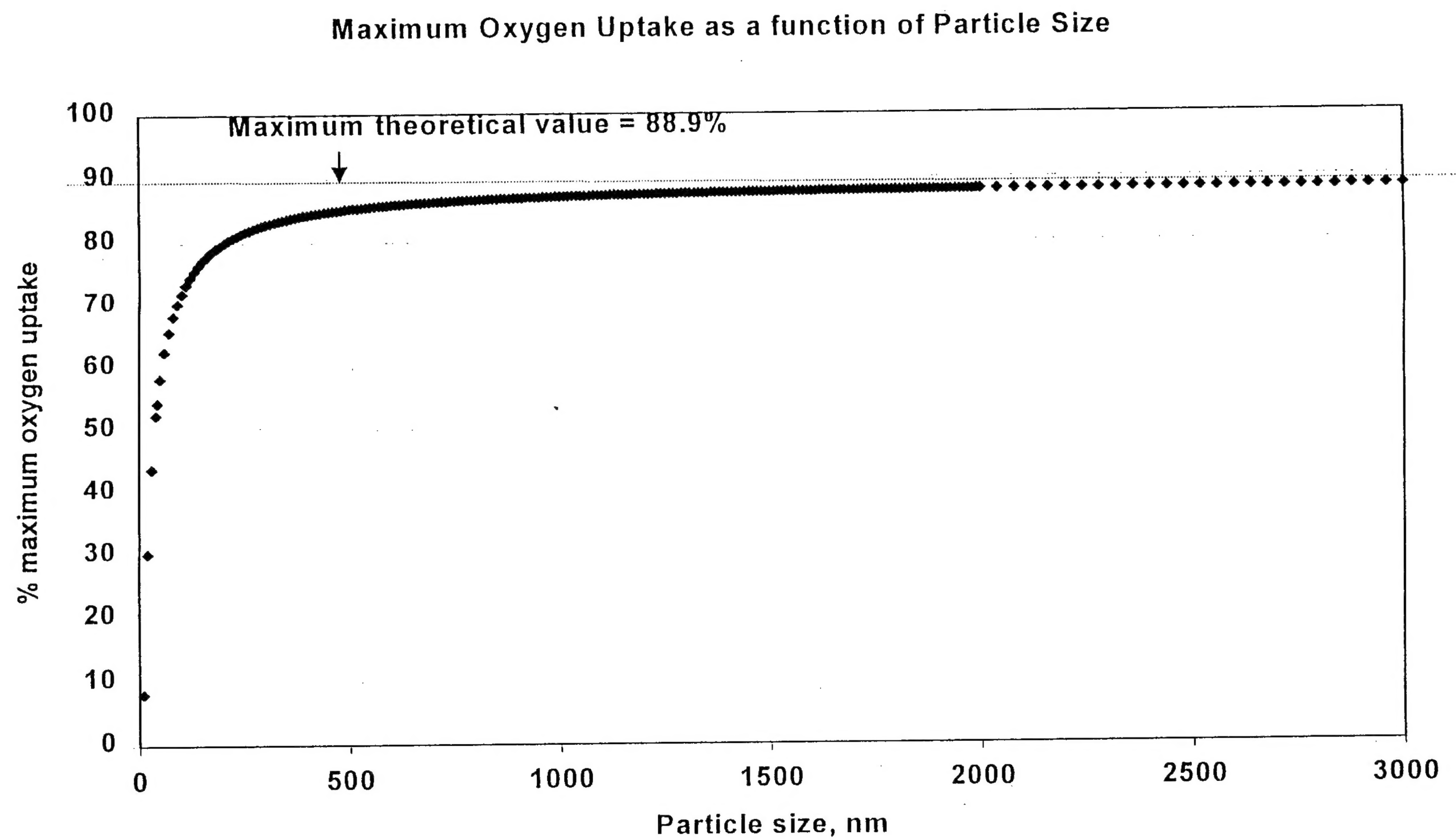
As particle size decreases, the percent of active aluminum decreases. Performance (ISP) of aluminized propellant may be lowered.

(Pre-existing oxide thickness is arbitrarily taken here as 2.5 nm)



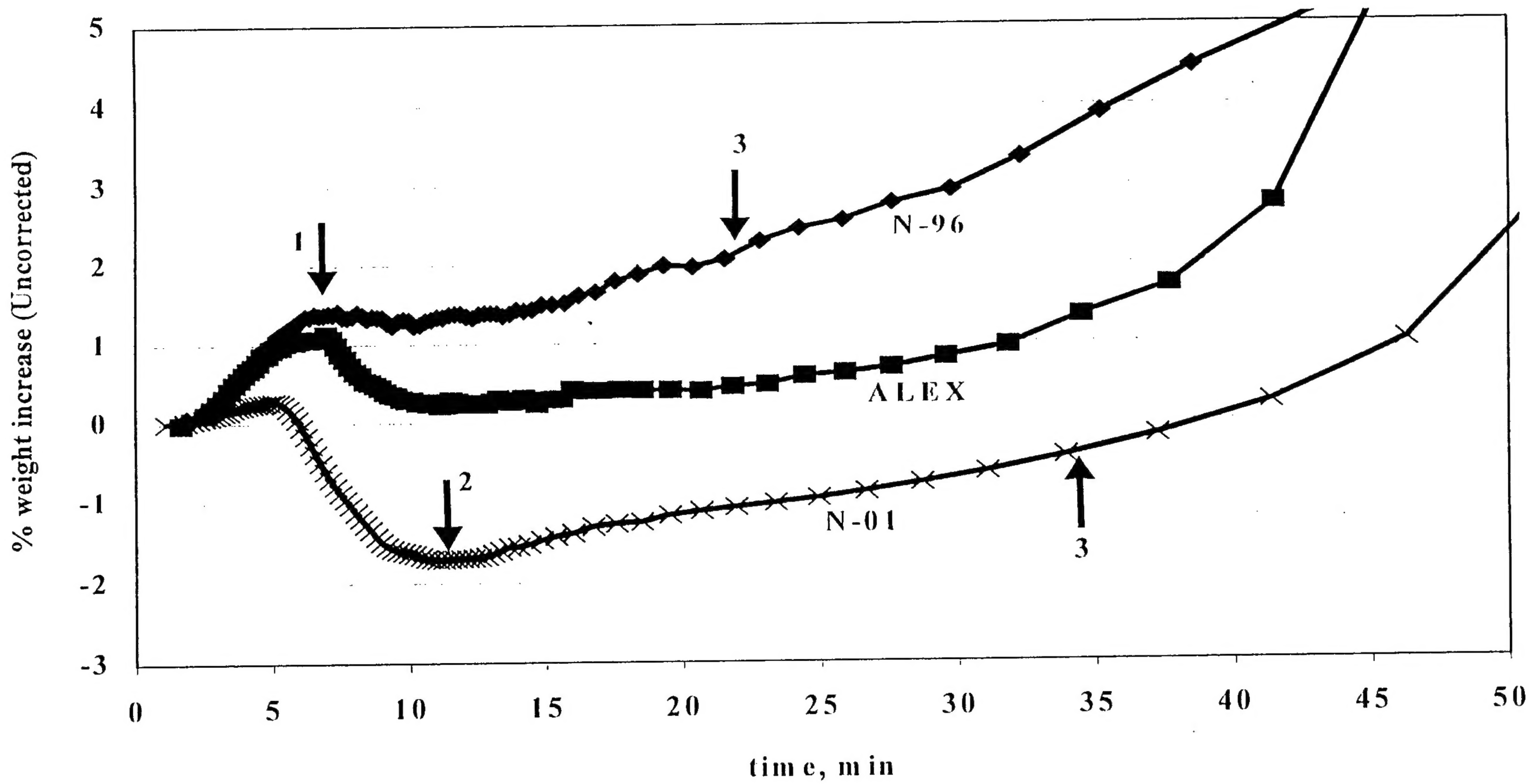
- **Recommend to develop a technique for thin coating the particles immediately after they are born.**

Theoretical oxidation of Al particles of different sizes with a constant starting (pre-existing) Al_2O_3 layer thickness = 2.5 nm



Based on the 2.5 nm assumption, UFAl particles have less active aluminum and requires less oxygen than the state-of-the-art aluminum particles.

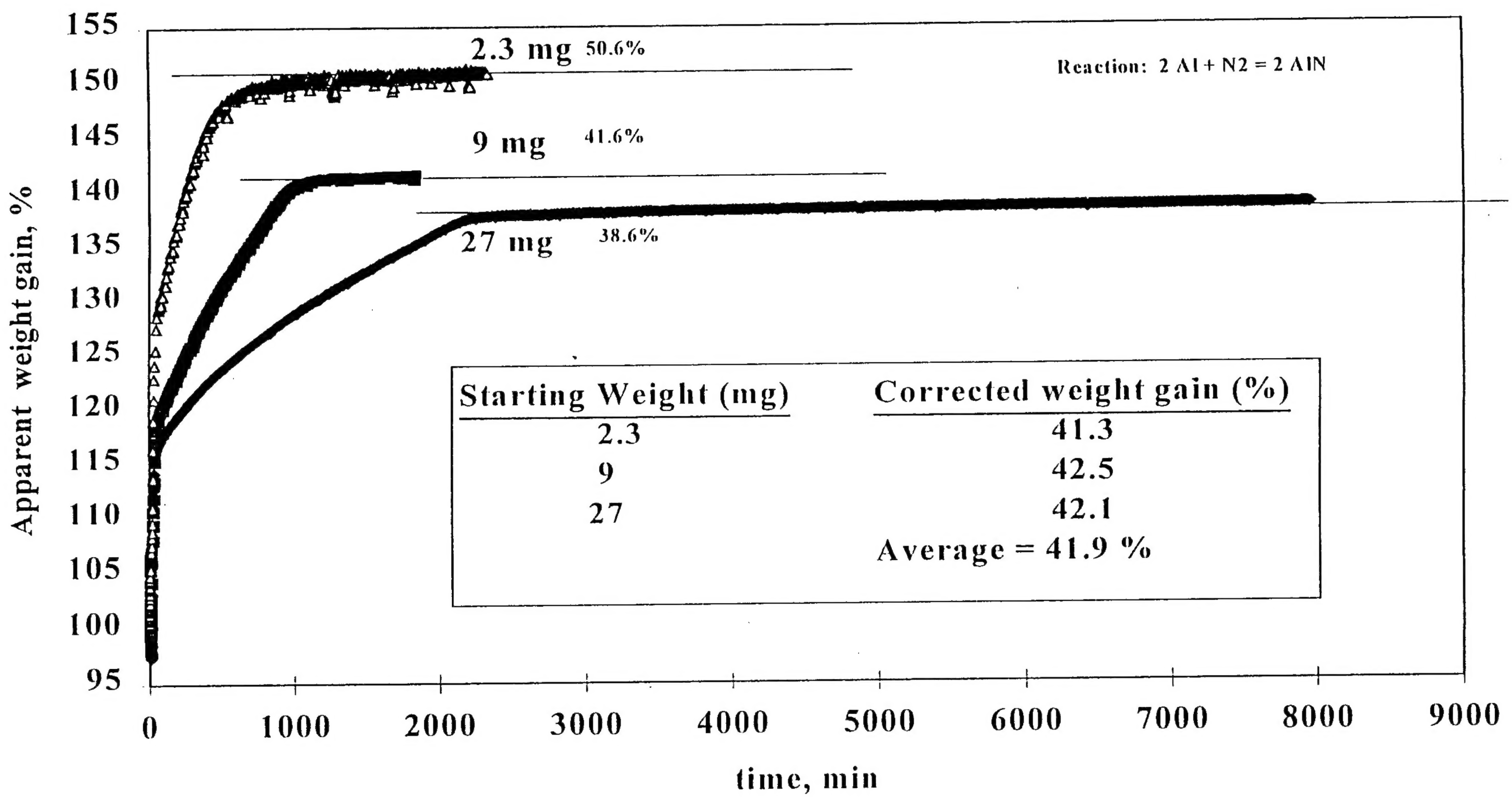
The nitridation reaction of UFAl powder at the early stages of heat-up includes three main steps: 1.Weight gain due to change in gas density (buoyancy effect). 2.Weight loss due to release of moisture and volatiles 3. Weight gain due to oxidation (or nitridation) plus buoyancy effects.



- Corrected weight gain = apparent weight gain + maximum weight loss - buoyancy effects

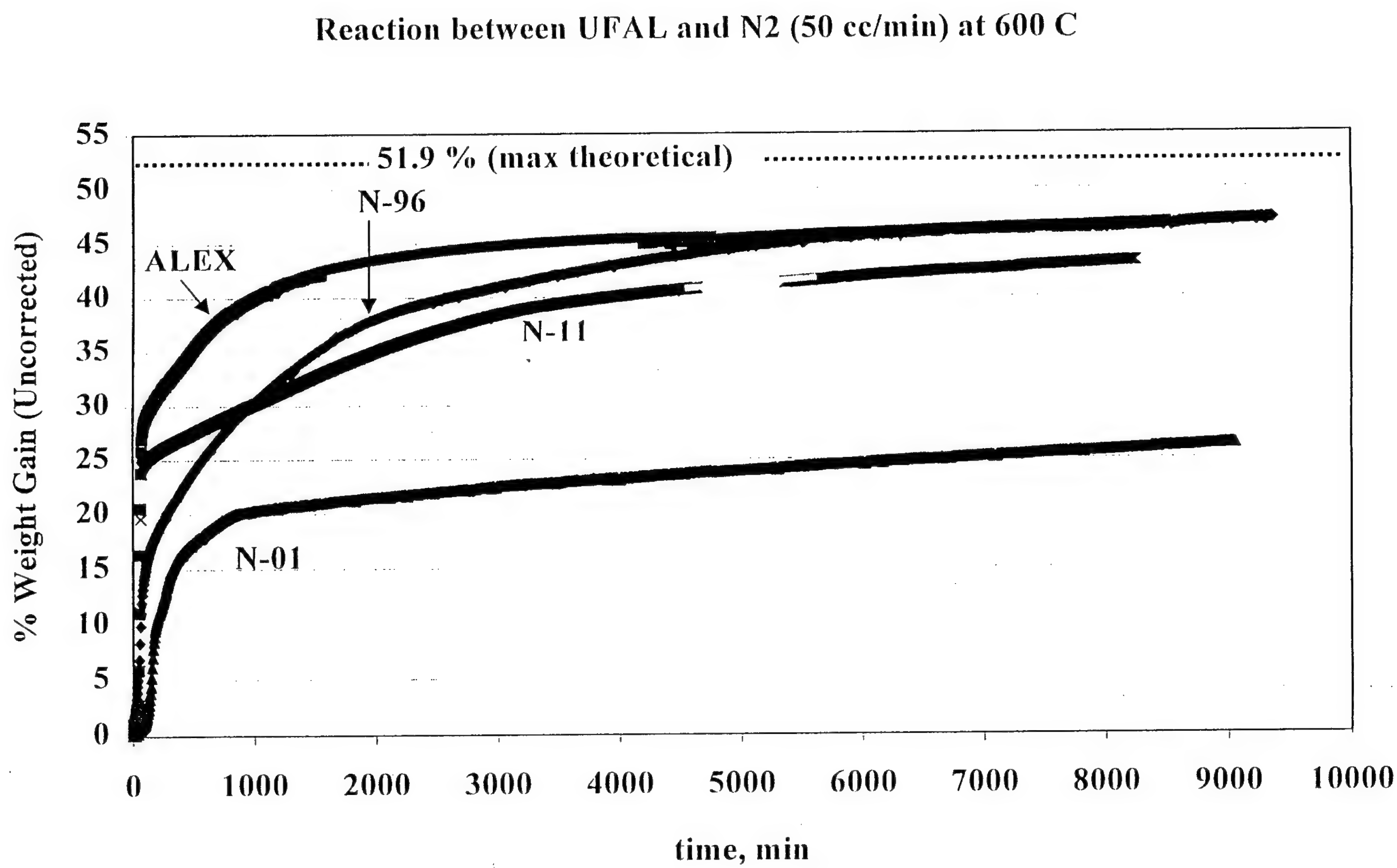
Apparent weight gain is a function of sample size: diffusion through UFAl bed is significant - smaller samples show excess weight gain

Effect of Al bed height at 600 C on kinetics (Indian Head UFAl powder)

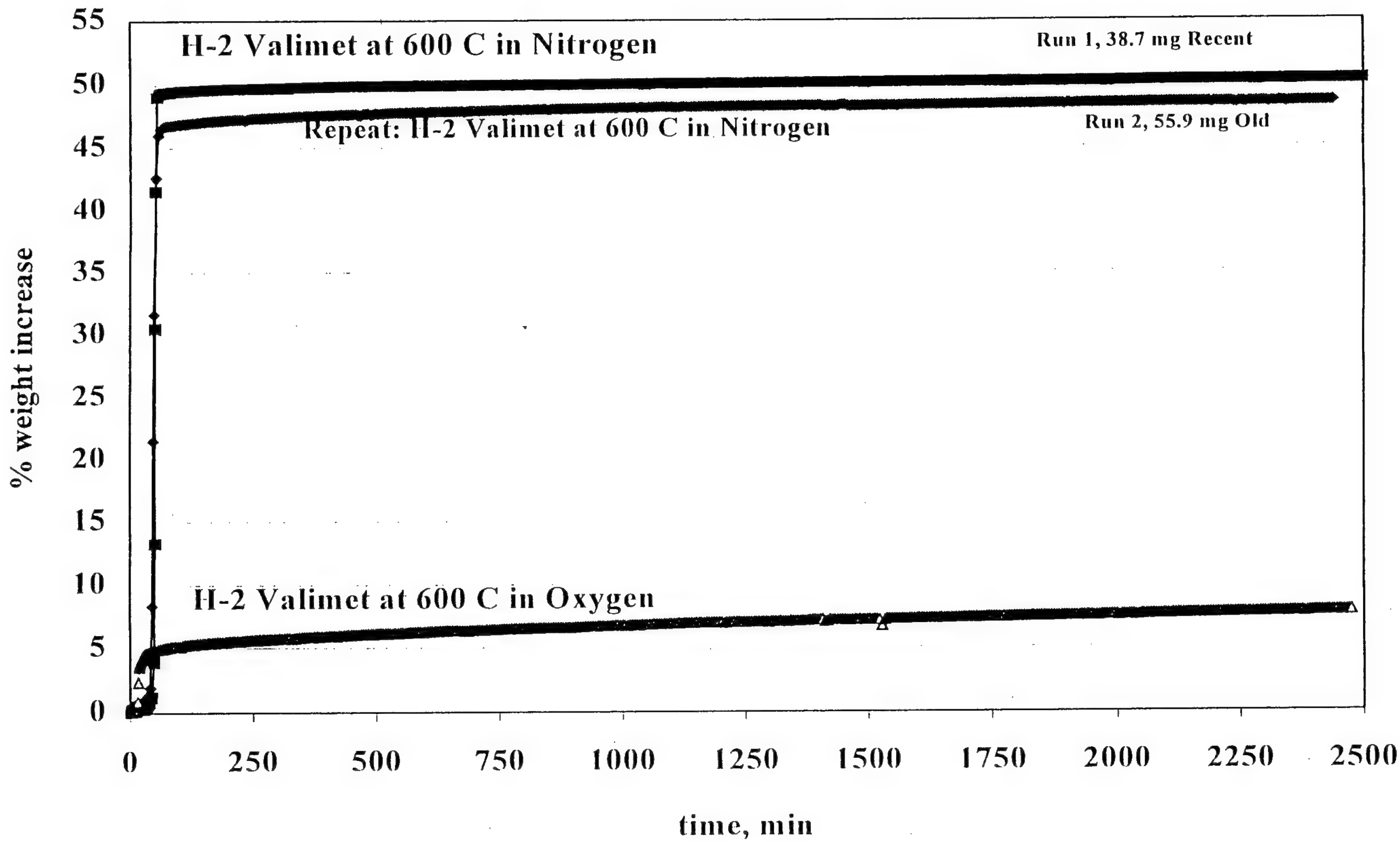


- The average corrected weight gain is independent of sample size
- Error = $\pm$ 0.6%

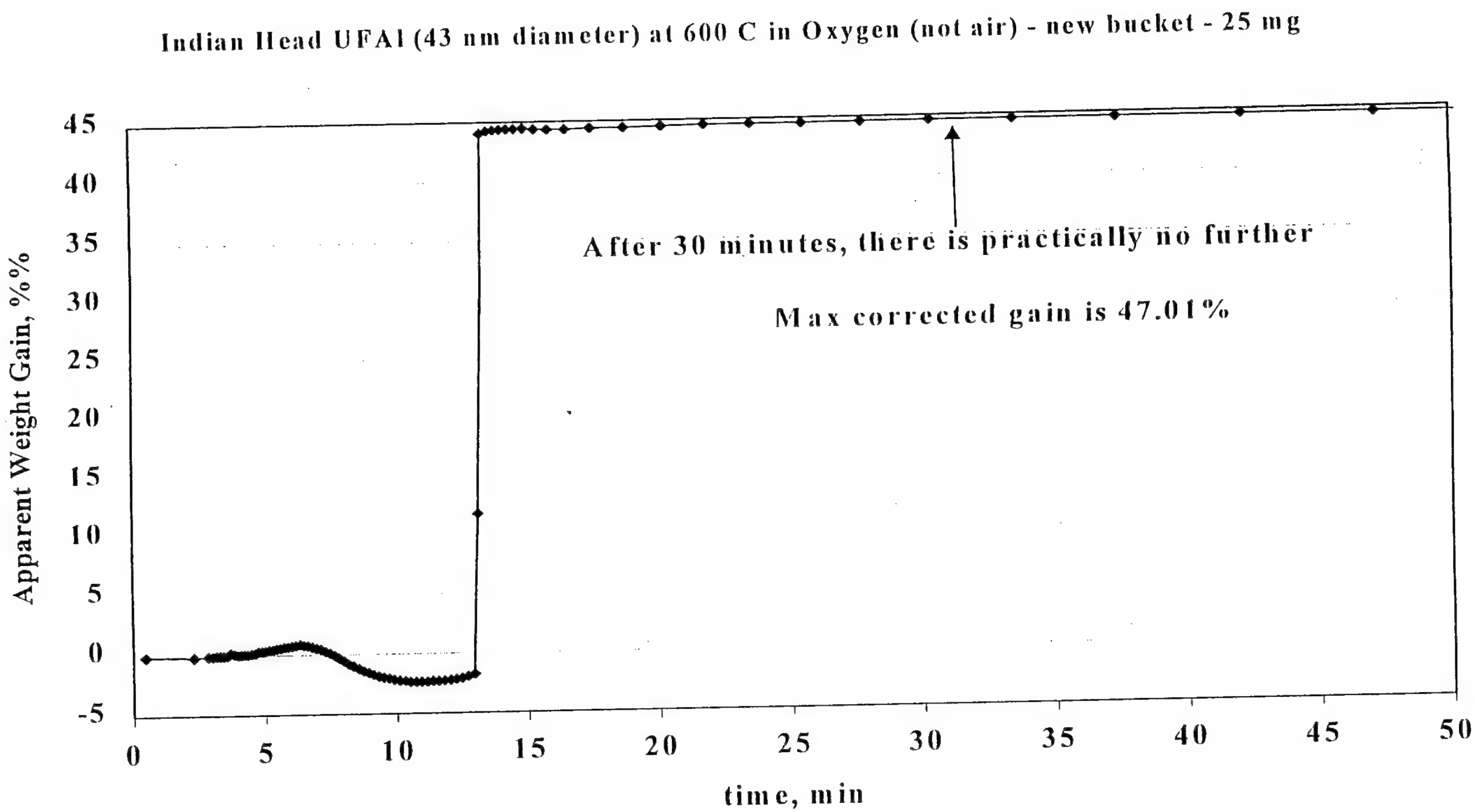
Nitridation reaction of UFAl



Nitridation and oxidation reactions of H-2 Valimet at 600 C.
In nitrogen, the reaction is completed in ~ 1 hour.
In oxygen, less than 10% of active aluminum was oxidized.

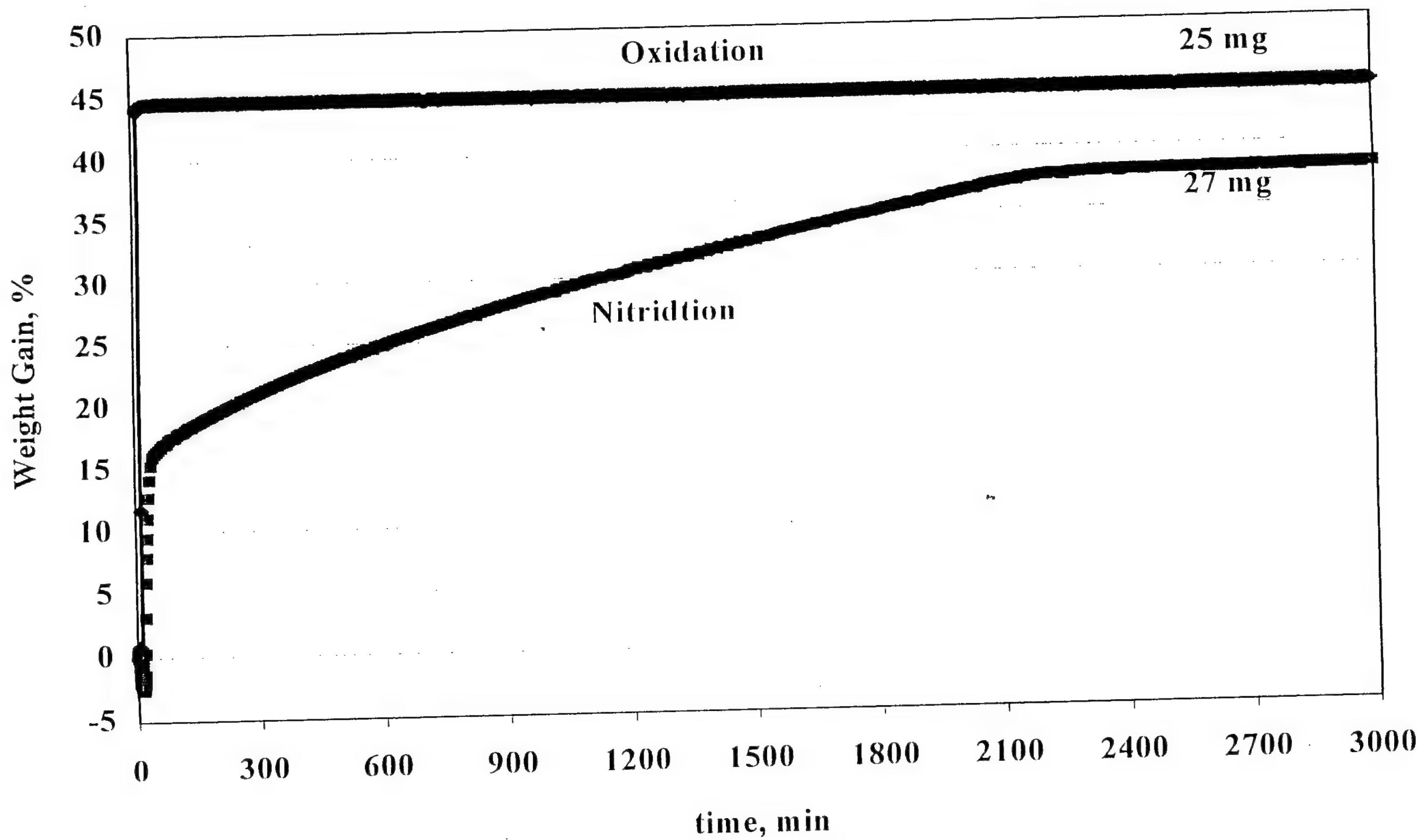


Oxidation of UFAl (43 nm diameter) in oxygen at 600 C



- The oxidation is completed in 15 minutes

Nitridation and oxidation reactions of UFAl-IH (43 nm) at 600 C.
In oxygen, the reaction is fast and reaches a constant value in ~ 30 minutes.
In nitrogen, the reaction is considerably slower.



Dr. Hawkins favorite page !!

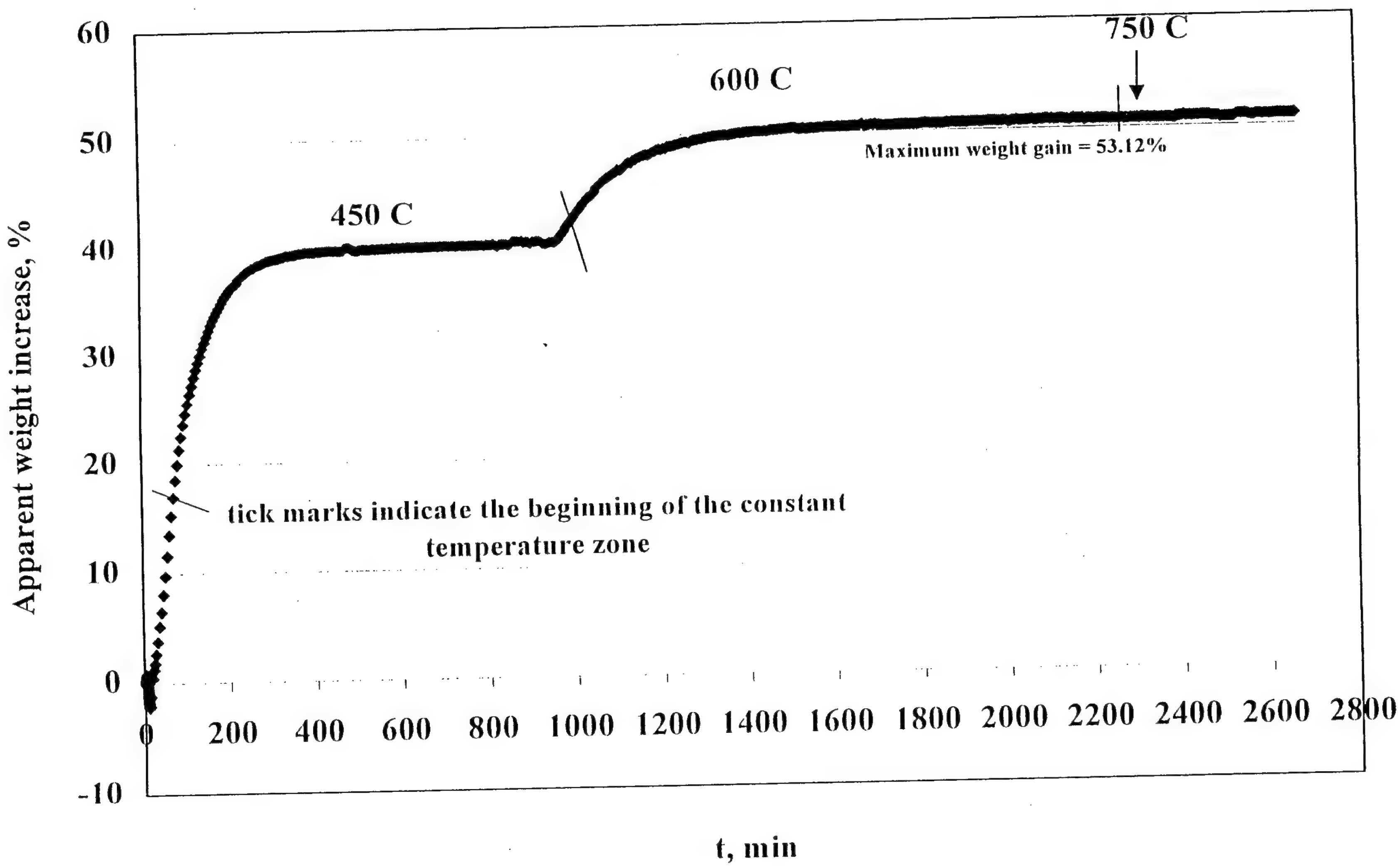
- The current work indicates that there exist different types of diffusion limitations on the oxidation and nitridation reactions. The rate determining step differs with each gas.
- Under similar reaction conditions, the rate determining step is strongly controlled by the starting particle size of Al powder.
- The diffusion of N_2 through AlN at 600 C does not impose limitations on the kinetics of the reactions. The nitridation of the largest particle size was completed in an hour.
- However, the diffusion of oxygen through Al_2O_3 does impose limitations which can be reduced by raising sample temperature. Smaller particles oxidize faster than larger particles (a result of the length of diffusion distance).
- Diffusion limitations of nitrogen through the aluminum bed can play an important role in nitridation kinetics. Such limitations are either due to a high (physical packing) density of the finer particles which limits the flow of species to active aluminum surface, or a high probability of forming agglomerates as a result of melting.

?

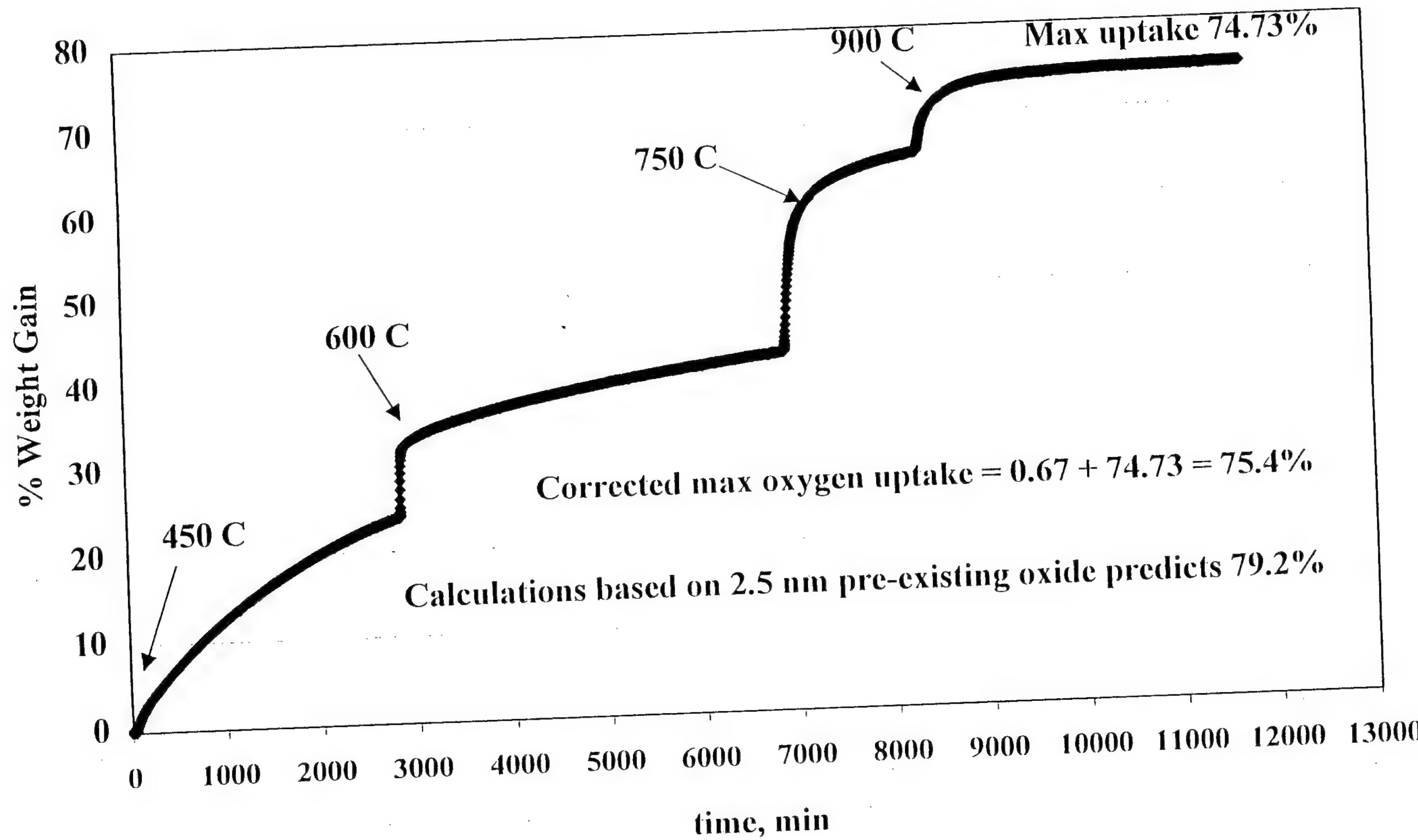
Tom will fix!

* THE VOLUME OCCUPIED BY PARTICLES IS INDEPENDENT OF PARTICLE SIZE FOR MECHANICAL ENGINEERS.
* WHAT DOES THIS MEAN IN REALITY?

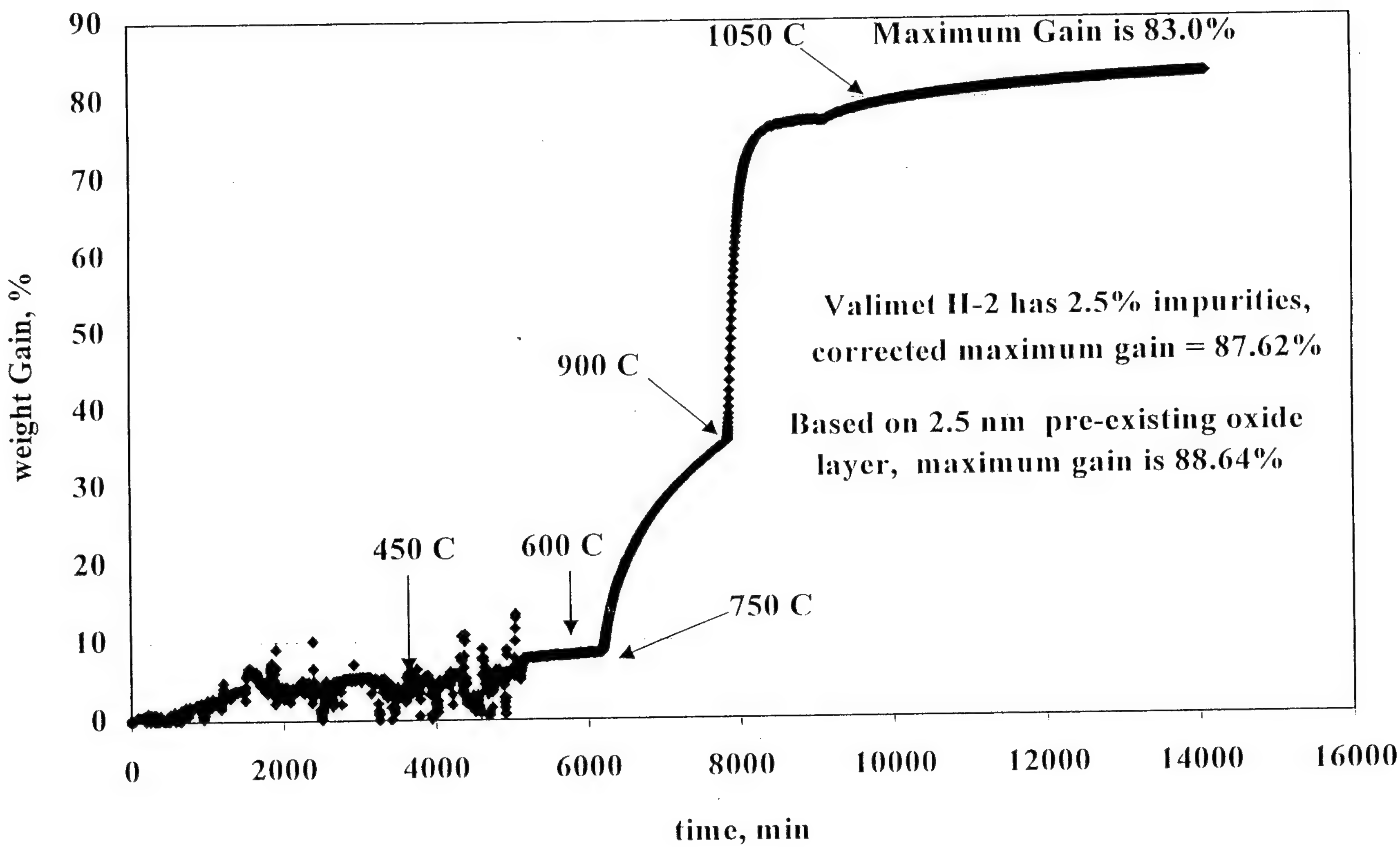
Step oxidation of UFAl-IH (46 nm) at different temperatures. With this particle size, the reaction is almost completed at 600 C.



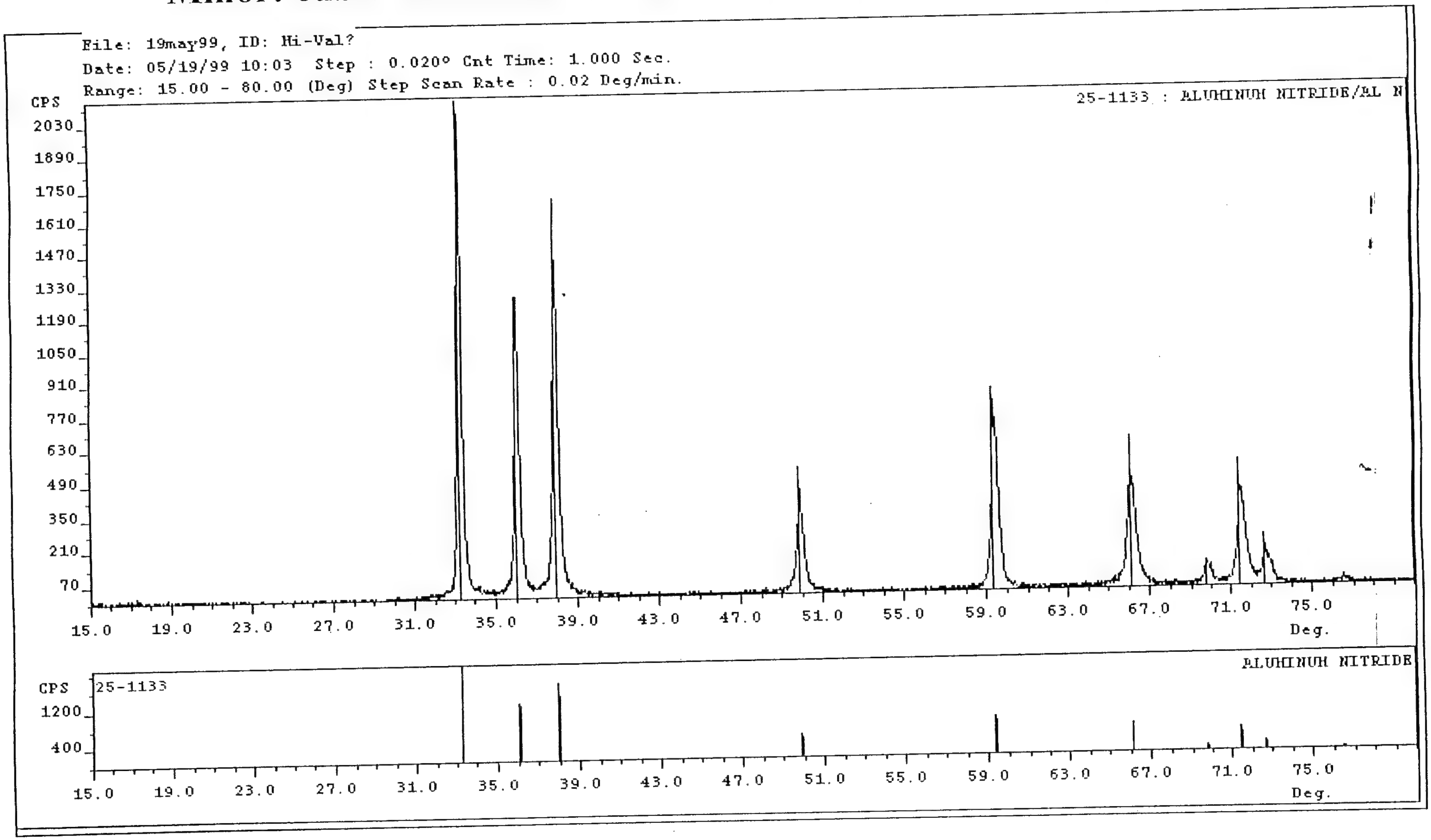
Russian ALEX (183 nm) in O_2 at 450, 600, 750 and 900 C: The reaction is almost completed ONLY at 900 C.



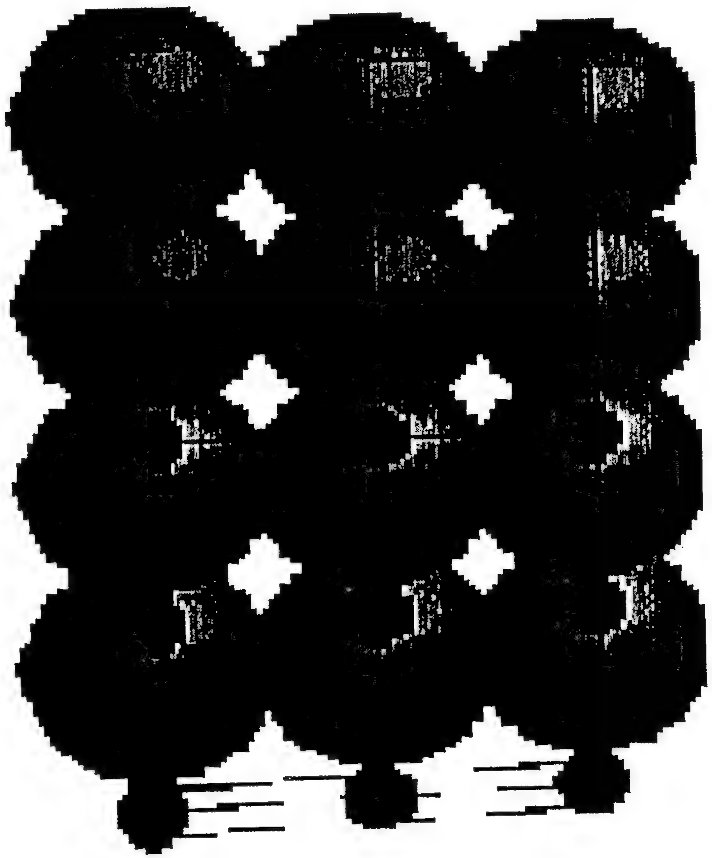
Valimet H-2 (1035 nm) in oxygen at 450, 600, 750, 900, 1050 C. The reaction is completed at 1050 C. Oxidation at 450 and 600 C is slow.



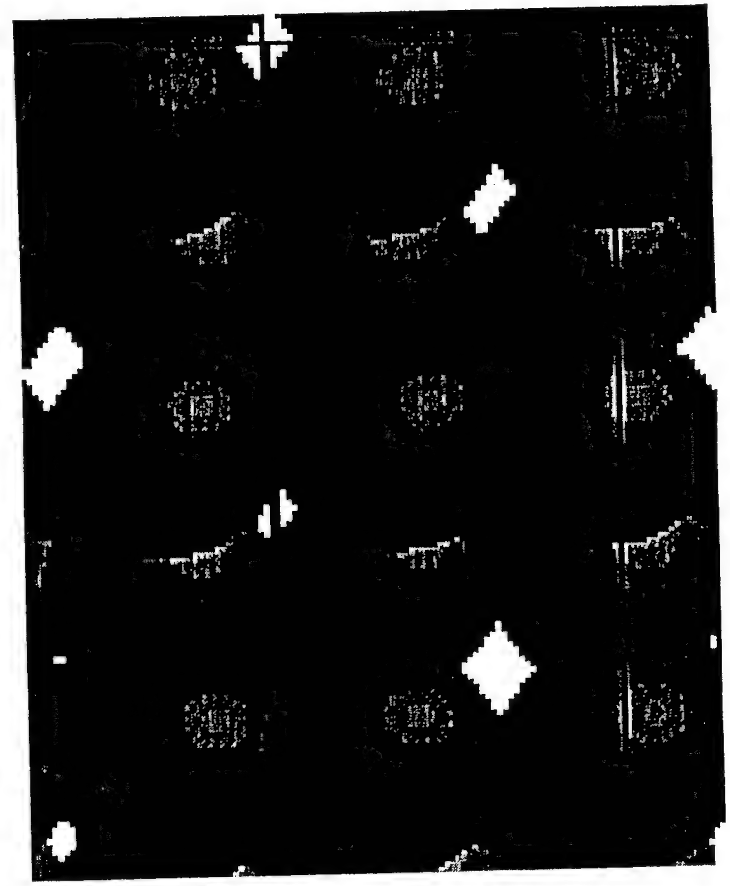
X-ray diffraction data on residue left after nitridation of Valimet H-2.
Major component: 95% + hexagonal aluminum nitride.
Minor: cubic aluminum nitride and cubic aluminum oxy-nitride.



Crystal structure of AlN and Al_2O_3: the nitride has more interstitial space than the oxide.



AlN



Al_2O_3

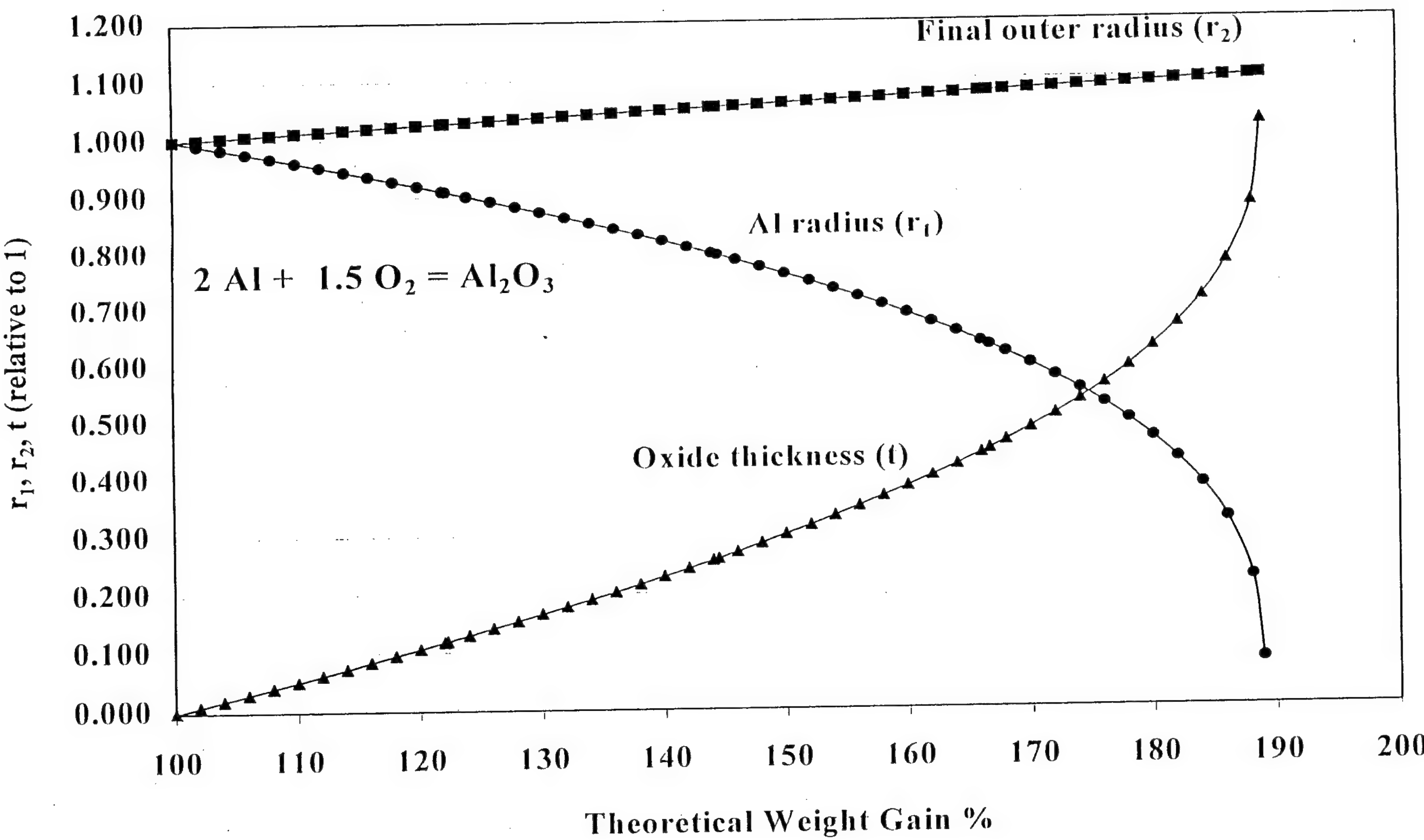
- The structures suggest that diffusion of gases through the oxide crystal is more restricted than through the nitride crystal.

Theoretical considerations and computations

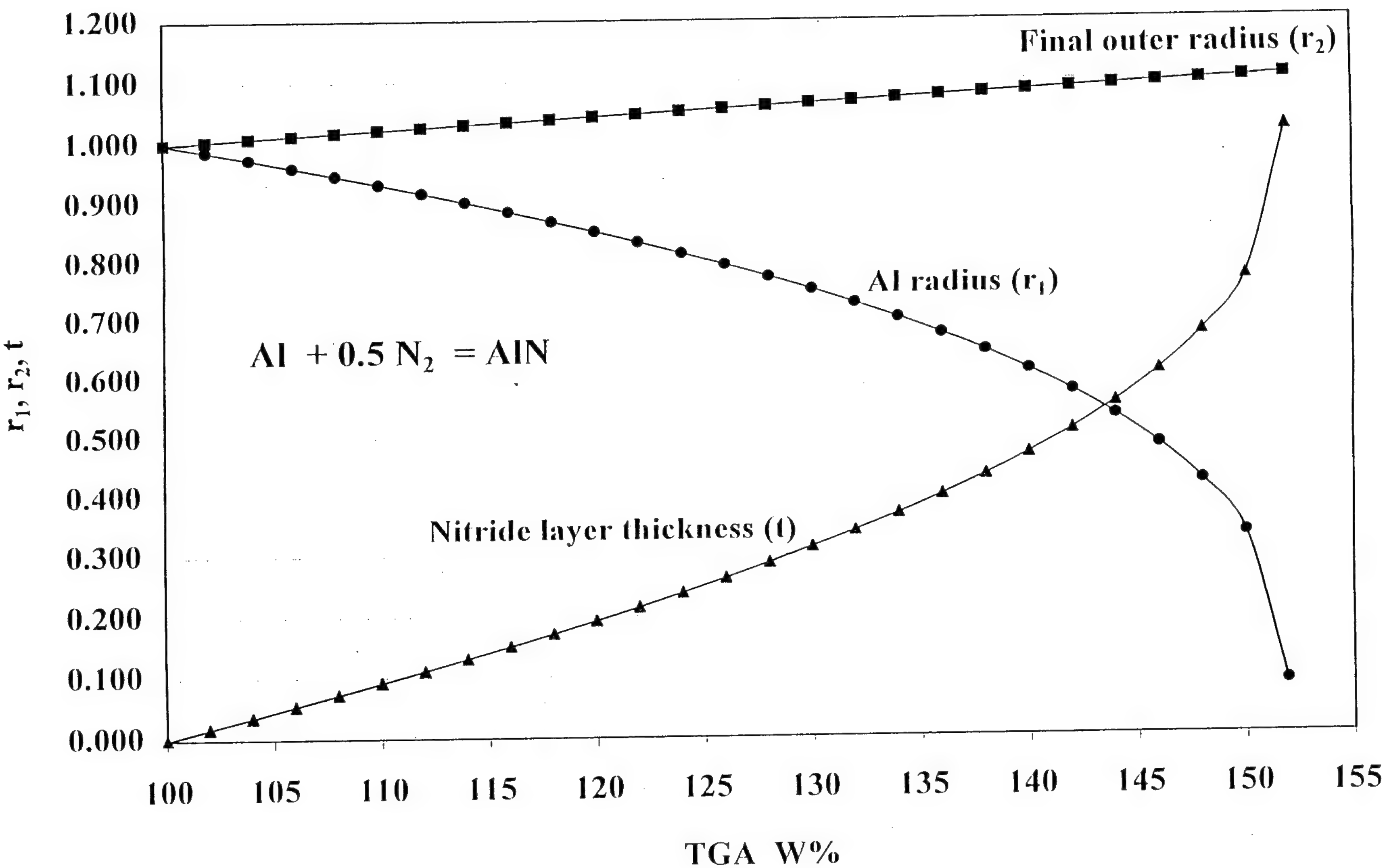
- When aluminum reacts with nitrogen or oxygen, the particles swell.
- All particles of different sizes have a pre-existing external Al_2O_3 layer covering a core of active aluminum.
- The thickness of the oxide layer is assumed constant for all particles. It is taken here as 2.5 nm.
- As the process propagates, the radius of aluminum core, r_1, decreases.
- At a given time interval, the radius of the entire particle (aluminum core + aluminum nitride layer + pre-existing Al_2O_3) is taken as r_2.

  Thus: $r_2 - r_1 - 2.5$ nm = thickness, t, of AlN (or Al_2O_3) formed during reaction.
- Densities of Al, AlN and Al_2O_3 were taken as 2.70, 3.26 and 3.84 g/cc.

Oxidation of Aluminum (starting particle size = 1.00 nm)



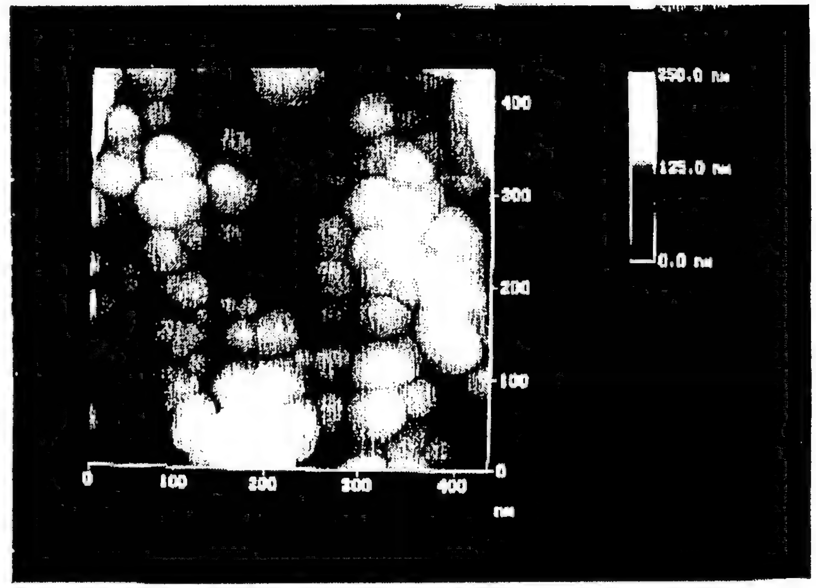
Nitridation of Aluminum (starting particle size = 1.00 nm)



STM Photos of UFAl-IH Powders

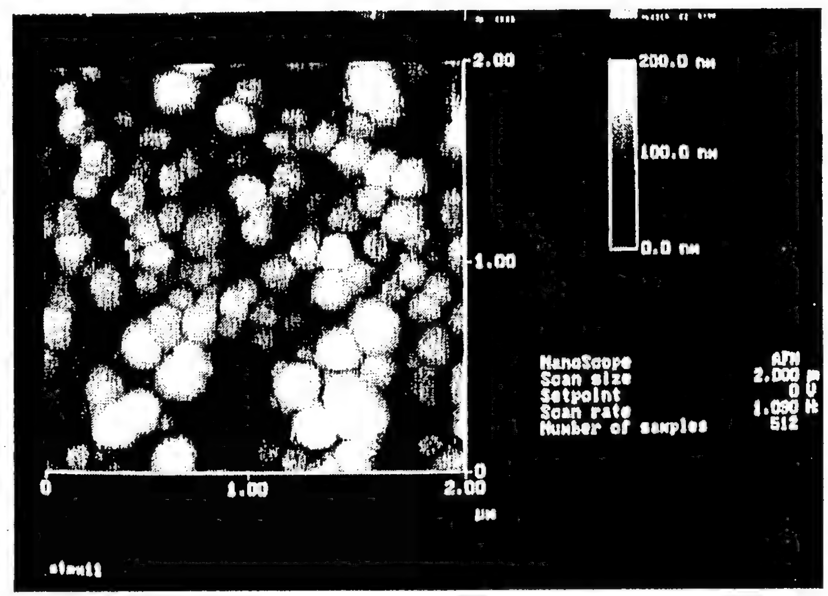
IH

Average size: 43 -64 nm

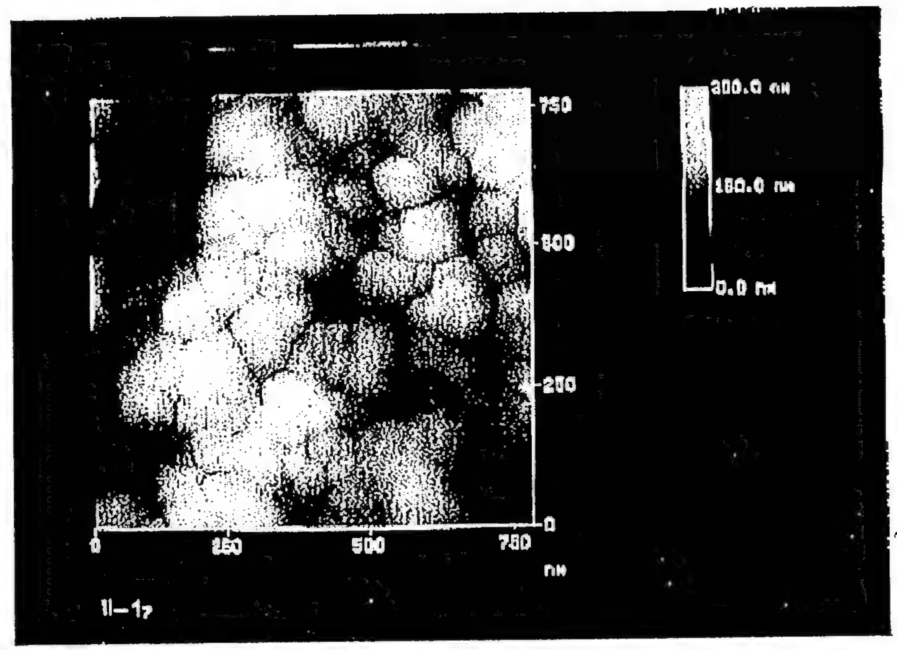


ALEX

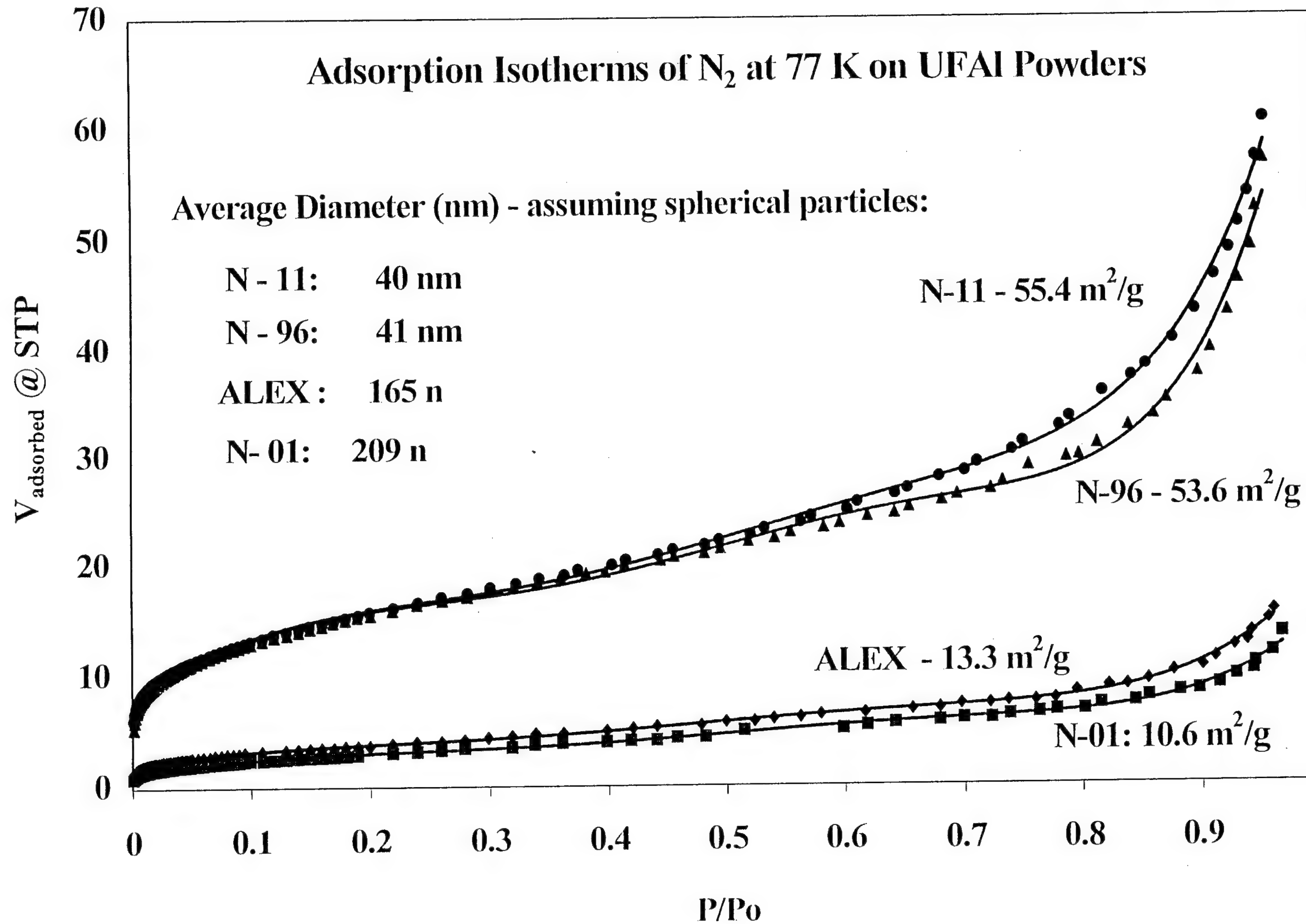
Average size: 160-190 nm



SEM and STM of AlN after complete nitridation of UFAl-IH powder.



The ultrafine particles agglomerates moderately during the nitridation reaction at 600 C. Individual particles are still seen.


Adsorption Isotherms of N2 at 77 K on UFAl Powders
Average Diameter (nm) - assuming spherical particles:
N - 11: 40 nm
N - 96: 41 nm
ALEX : 165 n
N- 01: 209 n
N-11 - 55.4 m2/g
N-96 - 53.6 m2/g
ALEX - 13.3 m2/g
N-01: 10.6 m2/g
V adsorbed @ STP
P/Po
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Surface Area and Estimated Average Particle Size for Ultrafine Aluminum Powders

Sample ID	Average A_s m^2/g	BET Average Particle size (nm)	Average Particle size from STM
ALEX	13.3	165	177
RF-A	48.1	46	40-120 nm (agglomerates)
RF-B	48.6	46	20-100 nm (agglomerates
Valimet H-2	2.14	1035 (~ 1 μ)	0.5-3.5 μ spherical
N-35	15.73	141	50-250 irregular shapes
N-40	6.87	322	50-100 irregular shapes
N-41	79.0	28	30-110 spherical
IH	51.3	43	43-64 spherical

Assumptions used to estimate particle diameter from BET surface area:

- Particles have insignificant porosity.
- Particles are composed of perfect spheres of one uniform size.
- Particles are smooth, they have zero level of roughness.
- Density of Al powders is = 2.71 g/cc.

Average particle diameter, d (in nm) was calculated from the BET surface area, A_s (m^2/g) using the following equation:

$$d \text{ (in nm)} = 6000/(2.71 * A_s)$$

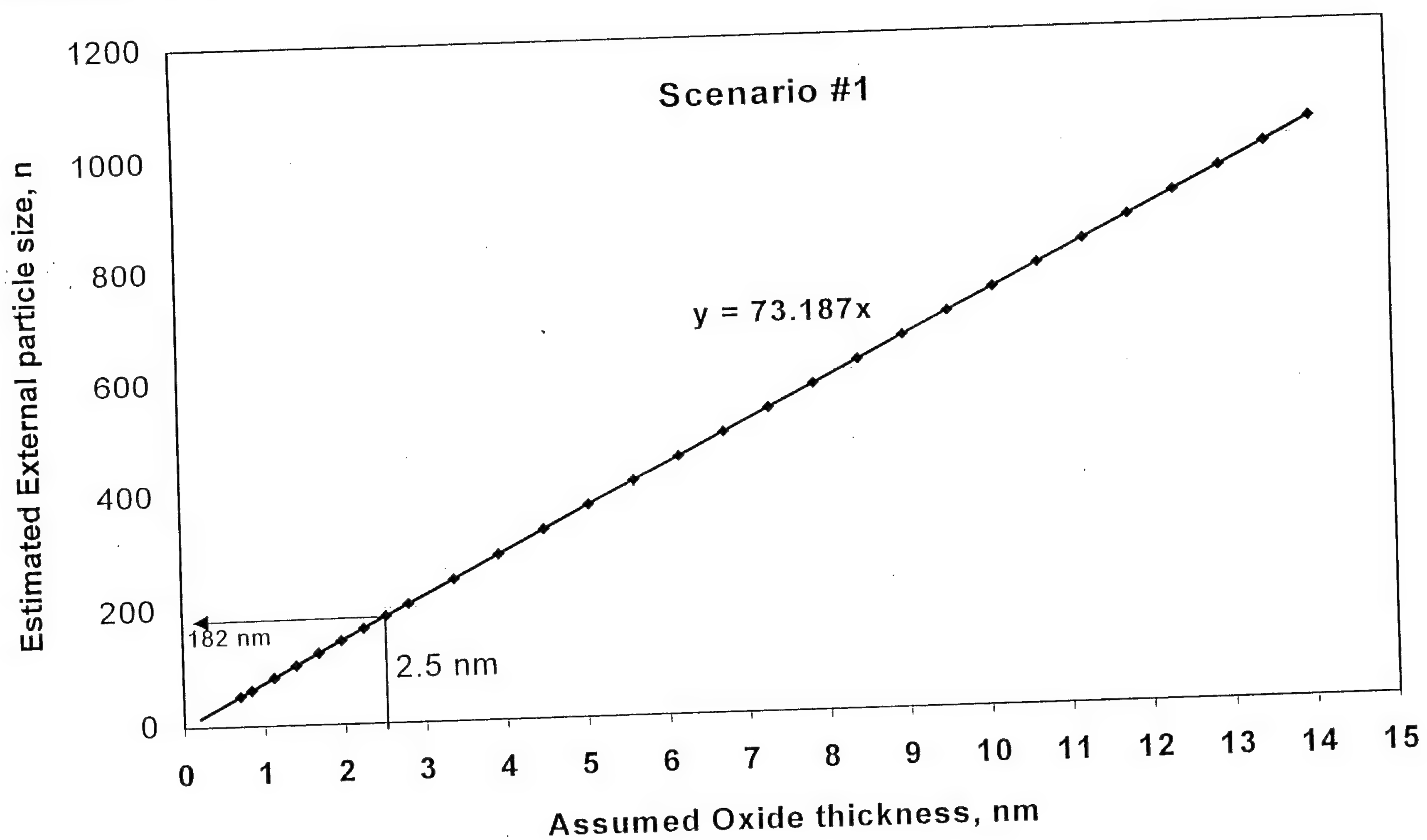
Different methods for determining particle size of UFAl powders

METHOD	Pros and cons
• Direct from STM and SEM	• Electrostatic causes agglomeration
• BET surface area	• All particles assumed spherical • Gives One average size • No roughness
• Direct from TEM cross-sections	• Work in progress
• From TGA measurements see next Three slides	• Need to know thickness of pre-existing Al_2O_3 layer

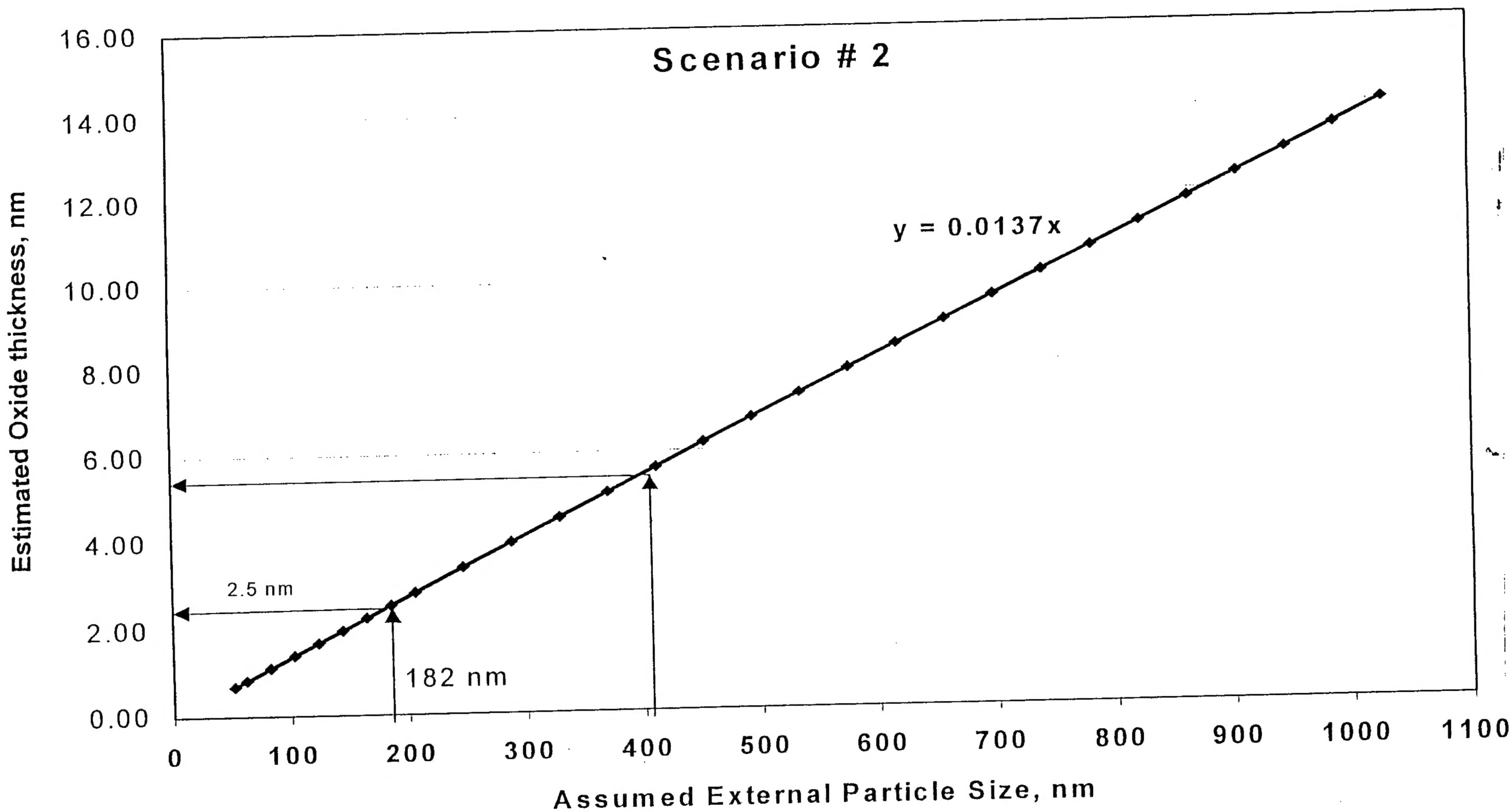
Dependence of percent active aluminum on UFAl starting particle size (nitridation reaction at 600 C)

Sample	BET size, nm	% Al	% Al_2O_3	Estimated thickness, nm
N-11	40	87.82	12.18	0.61
N-96	41	87.91	12.09	0.62
ALEX	165	89.21	10.79	2.22
N-41	28	85.67	14.33	0.51
RF-A	46	85.47	14.53	0.85
RF-B	46	94.83	5.17	0.29
IH				
IH-small	43	79.63	20.37	1.24
IH-medium	43	82.05	17.95	1.07
IH-large	43	81.13	18.87	1.14
	Average:	80.94	19.06	1.15
Valimet H-2	1035	92.19	7.81	9.92
ALEX-RUSSIAN	183	89.16	10.84	2.48

1. Find percentage of active aluminum (taken here as 90%) after complete nitridation.
2. Assume the balance (10%) as the pre-existing Al_2O_3 layer.
3. Obtain a plot between thickness of oxide layer and particle size.
4. Assume a value for the thickness (e.g., 2.5 nm) and obtain particle size.



1. **Find percentage of active aluminum (taken here as 90%) after complete nitridation.**
2. **Assume the balance (10%) as the pre-existing Al_2O_3 layer.**
3. **Obtain a plot between particle size and thickness of oxide.**
4. **Take the particle size of powder as computed by the BET previous calculation.**
5. **Obtain the corresponding oxide thickness from the plot.**



CONCLUSIONS

- Reaction between UFAl powders and nitrogen indicated that the nitridation reaction was completed at 600 C on all samples examined.
- The nitridation reaction forms hexagonal AlN as shown by x-ray diffraction.
- Diffusion of gaseous N_2 from the outer surface of particles through the AlN layer to the inner core of aluminum is not restricted at 600 C.
- Unlike nitridation, the reaction between UFAl powders and O_2 is not always completed at 600 C.
- The completion of oxidation reaction depends on UFAl particle size. For smaller particles (~ 50 nm), the oxidation can be completed at 600 C. For larger particles (~ 1000 nm), the oxidation can ONLY be completed at higher temperatures; as high as 1050 C.
- Diffusion of O_2 through the oxide layer to inner core of aluminum is restricted. The oxide layer is imposing diffusion limitations on oxidation.

RECOMMENDATIONS

- New techniques and methodologies are required to evaluate UFAl.
- Develop a technique for thin coating of UFAl immediately after the particles are born. This treatment will increase the active aluminum content of the sample.
- In order to evaluate the different methods of preparing UFAl powders, samples with different particle sizes ought to be prepared by each method.
- The effect of aging (for example, the exposure of UFAl powders to dry and wet air) needs to be addressed.
- Compatibility between UFAl powders and other propellants, fuels and oxidizers needs to be considered.

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